condenser and ground-glass joint fused onto a 50-ml flask. The vessel was attached to a vacuum line and evacuated while the sample was alternately cooled to −78° and warmed to room temperature to remove dissolved gases. A −78° trap was maintained in the system to trap out any volatile products. The pressure was then raised with dry nitrogen to approximately 510 mm and heating of the flask was initiated. Over a period of 9 days the temperature of the oil bath was raised to 235° and the pressure increased to 575 mm. During the last 24 hr of the test, compound I refluxed (bp (extrapolated to 575 mm) 205°).

A small amount of volatile material trapped out at −78° was tentatively identified as hexamethyldisiloxane by comparison of its gas-phase infrared spectrum with the published spectrum.[11] The mass spectrum, though weak, supported the same conclusion (calcd for $C_6H_{18}Si_2O$, 162; found, 162). The quantity of gas trapped out at −196° was too slight to identify positively. The presence of the hexamethyldisiloxane, however, suggests that it might have been hydrogen chloride from hydrolysis of trimethylchlorosilane. The mass spectrum was very weak but supported this conclusion (calcd for $H^{35}Cl$ and $H^{37}Cl$, 36 and 38; found, 36 and 38). These compounds could have resulted from hydrolysis of I or the decomposition products of I.

The material in the flask was found by the pmr and infrared spectra of the mixture to be mostly unchanged I plus II. By integration of the pmr resonances of the *N*-methyl protons of I and II, the mixture was found to contain approximately 4% II.

Results

After qualitative experiments indicated that, in the dehydrohalogenation reaction, less than the stoichiometric amount of trimethylamine resulted in an increased yield of the desired product, a series of 13 semiquantitative experiments such as the two given above was performed to define more closely the optimum conditions.

It was found, however, that changes in the relative proportions of the reactants altered the nature of the by-products as well as the product yield. The nature of the by-products, in turn, was found to have a profound effect on the difficulty in purifying the product. Thus, only trends could be gleaned from the experimental data. In particular, the yield of the desired product I would decrease as the mole per cent of trimethylamine decreased below or increased above about 75. Further, if the ratio of the number of moles of trimethylamine to the number of moles of hexamethyldisilazane was less than 1, the favored by-product would be bis(trimethylsilyl)aminobis(dimethylamino)borane (II) whereas a ratio greater than 1 would favor the by-product chlorobis(dimethylamino)borane. The by-product II, which will be the subject of a separate communication, is a waxy solid which sublimes as the product I distils and both contaminates the product and plugs the condenser preventing further distillation.

It was found that the waxy solid II could be prepared in high yield by direct synthesis and could then be used to prepare I *via* a hydrogen chloride cleavage reaction.[5] When a stoichiometric amount of hydrogen chloride was used, net yields of I as high as 65% were observed but the product was still contaminated by over 10% of II. Increasing the hydrogen chloride used to a 50% excess over the stoichiometric amount decreased the amount of II to approximately 5% of the distillable product but also decreased the net yield of I to about 50%. Further increases in the amount of hydrogen chloride employed to a 100% excess eliminated the contaminant II in the product but dropped the yield of I to approximately 15%. Consistent with the results found by Geymeyar and Rochow[3] for the congeners of I mentioned earlier, it was found that the compound possessed significant thermal stability. Surprisingly, however, the decomposition that did occur did not result in the formation of a borazine as was the case with bis(trimethylsilyl)aminodichloroborane.[12] Instead, after the pure compound I was exposed to temperatures in excess of 200° for 24 hr, the only decomposition product containing boron was approximately 4% II.

Discussion

The mechanism of the dehydrohalogenation reaction is not thoroughly understood, but, as Nöth stated, "...if the Lewis acidity of the boron halide and the Lewis basicity of the amine decrease, the 1:1 complex may not form at all or only in an extremely small concentration."[13] Thus, the decreased acidity of dichlorodimethylaminoborane (compared to trichloroborane) and the relatively low basicity of silicon-substituted amines such as hexamethyldisilazane[14] would indicate a reaction mechanism other than one involving formation of an adduct with hexamethyldisilazane. If the mechanism involves the protonolysis of a boron–chlorine bond,[15] hydrogen chloride could be released which could cleave a dimethylamino group from dichlorodimethylaminoborane or its trimethylamine adduct (or derivatives thereof) as a reaction competing with the formation of trimethylamine hydrochloride. The dimethylamine produced could then react with dichlorodimethylaminoborane to produce chlorobis(dimethylamino)borane or react with I to form II, thus explaining the presence of the two observed by-products.

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A Study of the Reaction of Sodium Dimethylamidotrihydroborate(1−) with Diborane

BY PHILIP C. KELLER

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We recently reported a new synthesis of μ-$(CH_3)_2NB_2H_5$ based on the reaction of $Na(CH_3)_2NBH_3\cdot 0.5C_4H_8O_2$ with diborane (eq 1).[1] Examination of this

$$Na(CH_3)_2NBH_3 + B_2H_6 \longrightarrow \mu\text{-}(CH_3)_2NB_2H_5 + NaBH_4 \quad (1)$$

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[1] P. C. Keller, *J. Amer. Chem. Soc.*, **91**, 1231 (1969).

system by boron-11 nmr showed that intermediate species were present; further work resulted in the isolation of the new compound sodium bis(borane)dimethylamide(1−), $Na(CH_3)_2N(BH_3)_2$.[2] This paper describes the nmr investigation of the course of eq 1 and the role of $Na(CH_3)_2N(BH_3)_2$ as a reaction intermediate.

Experimental Section

General Information.—Conventional high-vacuum and glove-bag techniques were used throughout this investigation. The solvents monoglyme (1,2-dimethoxyethane) and diglyme (bis(2-methoxyethyl) ether) were purified by standard methods and stored over lithium aluminum hydride in evacuated vessels. Boron-11 nmr spectra were obtained using a Varian HA-100 spectrometer equipped with a 32.1-MHz probe and standard accessories. Chemical shifts are in ppm relative to diethyl ether–boron trifluoride. Nmr studies were performed in nmr reaction vessels equipped with Kontes Teflon high-vacuum stopcocks for the easy addition of reagents and the removal of products for separation and characterization.

$Na(CH_3)_2NBH_3 \cdot 0.5C_4H_8O_2$ was prepared by the reaction of dimethylamine-borane with sodium hydride in monoglyme followed by crystallization with dioxane.[3] μ-$(CH_3)_2NB_2H_5$ was prepared according to eq 1 as previously described.[1]

Study of the Addition of Diborane to Sodium Dimethylamidotrihydroborate(1−).—In a dry nitrogen atmosphere an nmr reaction vessel was loaded with a 0.103-g (0.82-mmol) sample of $Na(CH_3)_2NBH_3 \cdot 0.5C_4H_8O_2$. The vessel was evacuated and 1 ml of monoglyme was added. The boron-11 nmr spectrum of this solution was recorded to confirm the purity of the reactant. Diborane was then added to the system in approximately 0.4-mmol increments and the nmr spectrum of the resulting solution was recorded after each addition.

The spectrum obtained after addition of the first 0.4 mmol of diborane (Figure 1) consisted of a strong quartet centered at +11.0 ppm, characteristic of $Na(CH_3)_2N(BH_3)_2$[2], and a considerably weaker triplet at −3.0 ppm and quintet at +42.0 ppm, assigned to $(CH_3)_2NBH_2$ and $NaBH_4$, respectively. The low intensity of the $NaBH_4$ resonance is caused by saturation effects. In addition, a weak unidentified signal was present on the low-field side of the $(CH_3)_2NBH_2$ resonance. The unidentified signal disappeared upon further addition of diborane. The formation of $(CH_3)_2NBH_2$ was confirmed by isolation and identification (infrared spectrum) in a separate experiment in which diglyme was employed as the solvent. Addition of further increments of diborane caused no change in the $(CH_3)_2NBH_2$ triplet but resulted in the appearance of signals due to dioxane-borane and to μ-$(CH_3)_2NB_2H_5$ and NaB_2H_7, which are products characteristic of the reaction of $Na(CH_3)_2N(BH_3)_2$ with diborane.[2] Attempts to isolate the small amount of unidentified byproduct associated with the lowest field nmr signal were unsuccessful.

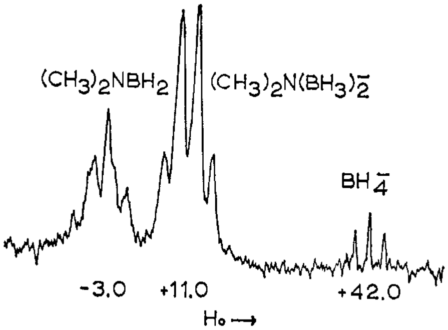

Figure 1.—Boron-11 nmr spectrum of a solution resulting from the reaction $Na(CH_3)_2NBH_3 + 0.5B_2H_6$.

Reaction of μ-Dimethylaminodiborane with Sodium Dimethylamidotrihydroborate(1−).—In a dry nitrogen atmosphere an nmr reaction vessel was loaded with 0.155 g (1.24 mmol) of $Na(CH_3)_2NBH_3 \cdot 0.5C_4H_8O_2$. The vessel was evacuated and cooled to −196°, and 1 ml of monoglyme followed by 1.25 mmol of μ-$(CH_3)_2NB_2H_5$ was added. The boron-11 nmr spectrum of the clear colorless solution formed after warming to room temperature showed a well-resolved triplet (−5.0 ppm) and quartet (+11.2 ppm) of intensity ratio 1:2, respectively. Assignment of the quartet to $Na(CH_3)_2N(BH_3)_2$[2] was confirmed by addition of diborane to the reaction vessel and subsequent isolation of μ-$(CH_3)_2NB_2H_5$ by high-vacuum methods. The presence of $(CH_3)_2NBH_2$ was confirmed by the boron-11 nmr spectrum of the monoglyme fraction of the volatile products.

Results and Discussion

Boron-11 nmr studies show that $Na(CH_3)_2NBH_3$ reacts with diborane to produce two principal sets of products. The first reaction (eq 2) results in addition of a borane group to produce $Na(CH_3)_2N(BH_3)_2$; the second lesser reaction (eq 3) results in formation of $(CH_3)_2NBH_2$ and $NaBH_4$. The latter products arise through the interaction of the starting reagents, possibly by a simple hydride ion transfer, and not by a process like eq 4; $Na(CH_3)_2N(BH_3)_2$ has not been observed to decompose in this manner.[2] The formation of μ-$(CH_3)_2NB_2H_5$ does not occur until more diborane is allowed to react with the $Na(CH_3)_2N(BH_3)_2$ (eq 5).

$$Na(CH_3)_2NBH_3 + 0.5B_2H_6 \longrightarrow Na(CH_3)_2N(BH_3)_2 \qquad (2)$$

$$Na(CH_3)_2NBH_3 + 0.5B_2H_6 \longrightarrow (CH_3)_2NBH_2 + NaBH_4 \qquad (3)$$

$$Na(CH_3)_2N(BH_3)_2 \not\longrightarrow (CH_3)_2NBH_2 + NaBH_4 \qquad (4)$$

$$(CH_3)_2N(BH_3)_2^- + B_2H_6 \longrightarrow \mu\text{-}(CH_3)_2NB_2H_5 + B_2H_7^- \qquad (5)$$

The reaction of $Na(CH_3)_2NBH_3$ with μ-$(CH_3)_2NB_2H_5$ suggests an alternate route to the formation of $(CH_3)_2NBH_2$ proceeding through the formation of a small quantity of μ-$(CH_3)_2NB_2H_5$ *via* eq 2 and 5 followed by reaction 6. This pathway seems less likely than eq 3, since $(CH_3)_2NBH_2$ always appears even when $Na(CH_3)_2NBH_3$ is in excess and since, as demonstrated by eq 5, diborane is superior to μ-$(CH_3)_2NB_2H_5$ when the two compounds are allowed to compete for a hydride ion.

$$Na(CH_3)_2NBH_3 + \mu\text{-}(CH_3)_2NB_2H_5 \longrightarrow (CH_3)_2NBH_2 + Na(CH_3)_2N(BH_3)_2 \qquad (6)$$

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Some Fluorocarbon-Bridged Ditertiary Phosphine Derivatives of Triosmium Dodecacarbonyl

BY J. P. CROW AND W. R. CULLEN*

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The development of a high-yield synthesis of triosmium dodecacarbonyl has stimulated research in this area.[1] Lewis and coworkers[2] have recently investi-

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